

# Chitosan Coated Copper-Oxide Film onto Si-wafer: A Novel Photo Catalyst for CO<sub>2</sub> Reduction

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**Abstract**— We report here synthesis, characterization and photo-catalytic behavior of chitosan coated copper-oxide nano catalyst towards reduction of carbon dioxide. The catalyst was synthesized by one-pot hydrothermal method using HCl depolymerized chitosan and CuSO<sub>4</sub> penta-hydrate salt. The purified catalysts were characterized by FTIR, AFM and XPS. A boron doped Si-wafer was spin coated with a thin film of aqueous dispersions of the catalyst and used for photo-reduction experiment with CO<sub>2</sub> under direct sun light for 5 hours. We observed formation of formic acid as a major photo-reduction product in FTIR analysis. We conclude combined Si-Wafer and Cu<sub>x</sub>O nano material is a promising photo-catalyst for CO<sub>2</sub> reduction.

**Keywords**—CO<sub>2</sub> reduction, photo catalyst, Chitosan coated -copper oxide.

## I. INTRODUCTION

During the recent years, there is an increasing interest [1-9] in the development of photo-catalysts and electro-catalysts for CO<sub>2</sub> reduction. Carbon dioxide is a greenhouse gas and causes global warming to a large extent. Natural photosynthetic pathway or carbon pathway [2] is not capable of restoring the ecological CO<sub>2</sub> balance because of rapidly increasing global carbon emission. Thus, CO<sub>2</sub> utilization through its photo-chemical or electro-chemical reduction [1-8] to alcohol or hydro-carbon is an additional effective path in restoring CO<sub>2</sub> balance. But major bottleneck of CO<sub>2</sub> reduction reaction is that it is thermodynamically non-spontaneous reaction and kinetically difficult because of requirement of high activation energy. In natural photosynthetic dark reaction, free energy released by conversion of ATP to ADP and reducing molecule NADPH are used to fix and reduce CO<sub>2</sub> to carbohydrate. The enzyme Ribulose Bisphosphate Carboxylase (RuBPCO) acts as catalyst. In laboratory experiments with CO<sub>2</sub> reduction using sun light or electrical energy, it is reported [2,8-9] oxides of copper, particularly Cu<sub>2</sub>O is an efficient catalyst for such reduction. This is because of its unique crystalline structures, where CO<sub>2</sub> molecules are easily adsorbed and calculated values of heat of adsorption show favorable interactions with CO<sub>2</sub> molecules. In this paper we report our work on preparation of copper -oxides nano particles and their applications in photo reduction of CO<sub>2</sub>.

## II. EXPERIMENTAL

### A. Materials

Low molecular weight Chitosan was purchased from Sigma Aldrich (Saint Louis, Missouri, USA) and used without further purification. CuSO<sub>4</sub>.5H<sub>2</sub>O, (technical grade) was purchased from CQ concepts INC (Ringwood, Illinois, USA). NaOH (ACS grade, Amresco Solon, Ohio, USA) and HCl (technical grade, Fisher Scientific.) were used as supplied. Hydrothermal reaction was carried out in a hard glass bomb keeping in a temperature controlled oven (Thermo electron corporation, Lundeberg/Blue M). A Mettler Toledo, Delta 320 pH meter was used to adjust pH of the solution after calibrating it using HACH pH calibration solutions. Barnsted Nano pure Diamond DI water system was used to obtain DI water of resistivity 17.9MΩ-cm. Fisher scientific Digital vortex mixer was used to mix reagents for reaction.

### B. Method

#### 1) Preparation of chitosan coated copper-oxides nano particles by hydrothermal method.

In this preparation of CS coated Cu<sub>2</sub>O/CuO, we used HCl as depolymerizer, 300 mg of chitosan was taken in a hydrothermal bomb to which 30 ml of 1% HCL in DI water was added, shaken well and kept at 150<sup>o</sup> C under hydrothermal condition for 0.5 hours, after the reaction the solution was cooled to room temperature and 25 ml of (1% w/v) CuSO<sub>4</sub> solution was added to the hydrothermally depolymerized solution and kept under vortex for one hour followed by addition of 1N NaOH drop wise to adjust its pH to 7.4. Then, 5ml of this solution was added to 25 ml DI water and kept under hydrothermal at 150<sup>o</sup>C for one hour to convert remaining Cu (OH)<sub>2</sub> completely to Cu<sub>2</sub>O/ CuO. The final dispersed solution was dialysed centrifuged and dried under vacuum for further studies.

## III. CHARACTERIZATION

Fourier Transform Infra-red Spectroscopy (FT-IR): FT-IR technique was used to characterize functional groups present in these four samples. FT-IR spectra were recorded on Perkin Elmer Spectrum 100 ATR FT-IR Spectrometer.

A. AFM Images

Silicon wafer (boron doped) was purchased from Nova electronic materials water dispersed sample was spin coated and dried in vacuum. AFM images were recorded on a Veeco Manifold multimode V model (tapping mode) using silicon nitride tip (radius B 50 nm) attached to a cantilever (spring constant = 0.032 Nm, oscillating frequency 0-600 k Hz). AFM images were recorded at room temperature.

B. TEM Images

FEI Tecnai TEM with resolution 0.20 nm point to point, 0.102 nm per line was used. The machine was equipped with SEG with hot and cold stages and High angle annular dark field (HAADF) detector using Gatan Image Filter (GIF). The lyophilized catalyst powder was dispersed in ethanol. Au grid with carbon mass was directly dipped in to the solution and after absorption was dried under vacuum for 24 hr to remove any solvent.

C. XPS images

X-Ray Photoelectron Spectroscopy (XPS) was performed on a Physical Electronics 5400 ESCA spectrometer equipped with a monochromatic Al K $\alpha$  source operating at 300 W. Vision software provided by the manufacturer was used for data analysis and quantification. A Shirley background was used for quantification and curve fitting of Cu2p, C1s, N1s and O1s spectra. All the spectra were charge referenced to the aliphatic carbon at 285 eV. For curve-fits, 70% Gaussian/30% Lorentzian line shape was used.

D. Fabrication of catalyst coated Si-wafer and photo reduction set up

1cm<sup>2</sup> silicon wafers was cut and cleaned with dilute HCl, water and ethanol followed by air drying. Chitosan coated copper nano particles disperser in water was spin coated at exact same condition as the AFM samples were prepared. In a 250 ml conical flask measured amount of Na<sub>2</sub>CO<sub>3</sub> was taken. Silicon wafers were drop casted with catalyst and were placed in 20 ml glass vial. The whole 20 ml vial open vials were then

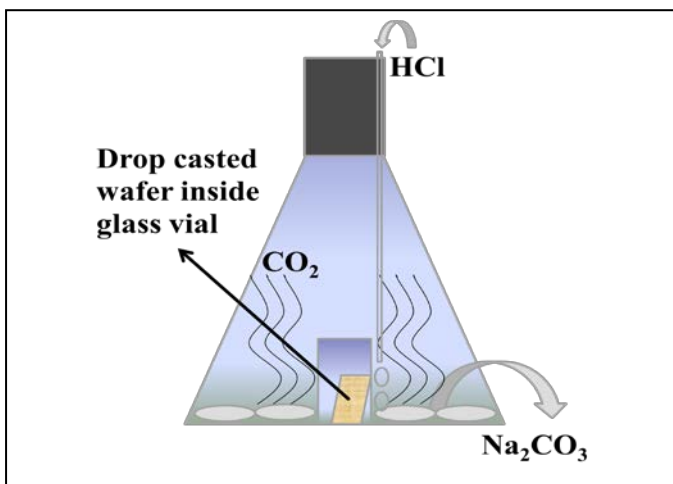


Fig. 1. Schematic diagram of experimental setup used to study photo reduction of CO<sub>2</sub> to methanol.

placed carefully in the conical flask so that Na<sub>2</sub>CO<sub>3</sub> solution kept for generating CO<sub>2</sub> gas remains separated. HCl was injected for full neutralization of Na<sub>2</sub>CO<sub>3</sub> inside. The whole set up was kept for 5 hr under direct sun-light. A control experiment was performed wrapping the container with a black paper.

IV. RESULTS AND DISCUSSION

FT-IR of CS coated copper oxides is shown in Fig.2. Presence of chitosan as coating material (2922 cm<sup>-1</sup> from characteristic C-H stretching from chitosan coating) is indicated. The -OH stretching frequency is reduced at 3380 cm<sup>-1</sup> may be due to binding of -OH groups to the metal ions. Again there is a blue shift in the chitosan amide (I) 1659 cm<sup>-1</sup> and amide (II) at 1503 cm<sup>-1</sup> indicating -NH ligand binding to copper nano particles.

The XPS spectra (Fig. 3) shows presence of different mixed valent copper both Cu<sup>+</sup> and Cu<sup>++</sup> copper oxide samples. The presence of small 934 ev peak is characteristic to Cu (I) where as the peak at 936 ev together with shake up peaks indicates presence of Cu(II) peak as well as chitosan coated NP.

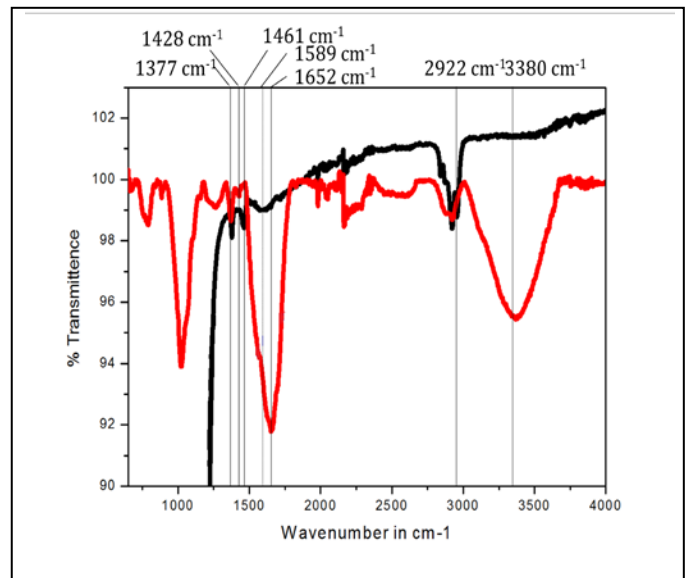


Fig. 2. FTIR of CS coated Cu-Oxides (black) and CS (red).

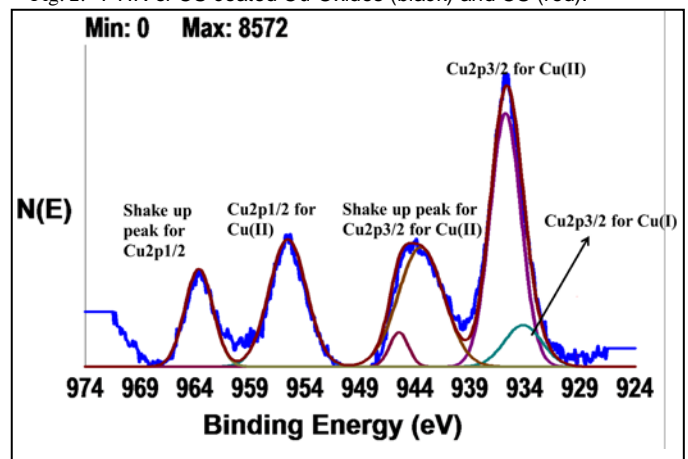


Fig. 3. XPS image of copper-oxide catalyst.

The AFM image (Fig. 4) clearly shows mono dispersed nano formation. Also these perfectly water soluble copper nano particles remain de-agglomerate because of electrostatic repulsion of  $\text{NH}_3^+$  groups present in chitosan coating at DI water pH (~6.3) as well as hydration layer above chitosan coating. The particle size varied from 400-500 nm which is basically Chitosan polymer with copper QDs embedded in the film like structure vertical distance (~ 20 nm). This is been confirmed from TEM image latter. The chitosan droplets were more spherical after drying in to air.

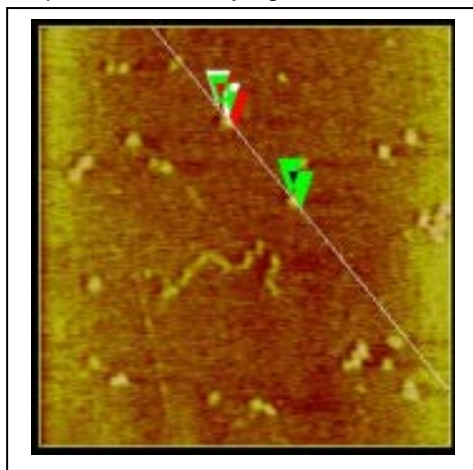


Fig. 4. AFM image of the prepared Cu-oxide catalyst.

From TEM image (not shown) we have seen the presence of copper QD in chitosan film. The d spacing was  $4.2\text{\AA}$  clearly matching with  $\text{Cu}_2\text{O}$ , 111 planes. It is worth mentioning that 111 plane is most efficient for catalytic reduction of  $\text{CO}_2$ . The diameters of the  $\text{Cu}_2\text{O}$  nano particles varied from 10-20 nm indicating formation of nearly mono dispersed quantum dots of  $\text{Cu}_2\text{O}$ .

The chitosan coated copper catalyst solution was drop casted on to the Si-wafer. It nicely stuck to the wafer owing to its film forming ability. The copper quantum dot were well coated but at the same time separate and exposed in to the stretched film as seen in AFM images. After exposing the catalysts coated Si-wafer to direct sunlight for 5 hours and analyzing the products by FTIR (Fig.5) with due pre treatment, we get an enhancement of -OH and -C=O stretching frequency after exposure to sun-light indicating formation formic acid as photo-reduction product of  $\text{CO}_2$ . It may be mentioned that Liu et al [8] using  $\text{TiO}_2$  catalyst also reported formation of formic acid as photo-catalytic reduction product.

Admittedly, the quantum yield of such conversion is extremely small but signature of formic acid is indicated from simple FTIR analysis. It may be mentioned that the reaction was carried out onto catalyst coated solid surface under moist condition in order to avoid huge -OH peak in this simple FTIR product analysis.

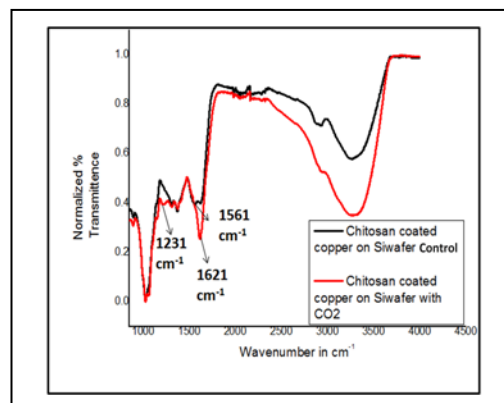
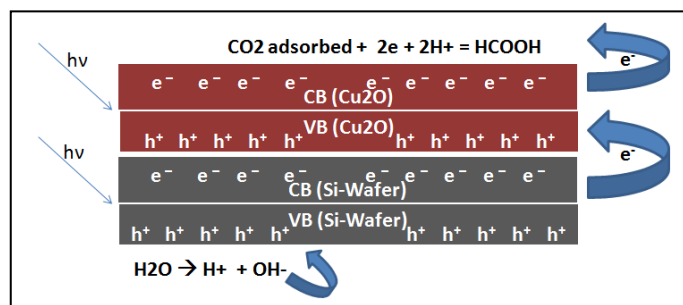


Fig. 5. FT-IR spectra of products onto si-wafer surface.

We propose a probable mechanism of formation of formic acid by the following scheme which is analogous to Z scheme of photo-synthesis reaction initiated by water splitting reaction [9] onto Si wafer .But unlike photo



synthesis here  $\text{CO}_2$  reduction is a light reaction.

## V. REFERENCES

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